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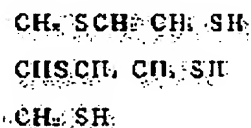
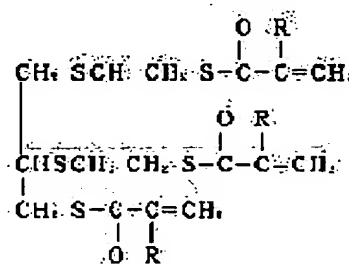
SUZUKI YORIYUKI

(54) SULFUR-CONTAINING (METH)ACRYLATE ESTER AND ITS USE

(57)Abstract:

PURPOSE: To obtain a novel sulfur-containing acrylate which is useful for glass lenses because it gives lenses excellent in optical characteristics, particularly having high refractive index and excellent in scratch resistance.

CONSTITUTION: This compound is represented by formula I (R is H, methyl). The compound of formula I is prepared e.g. by reaction of 1,2-bis [(2- mercaptoethyl)thio]-3-mercaptopropane of formula II with (meth)acryloyl chloride in the presence of a base such as triethylamine in a solvent such as hexane or THF at -20 to 60° C.



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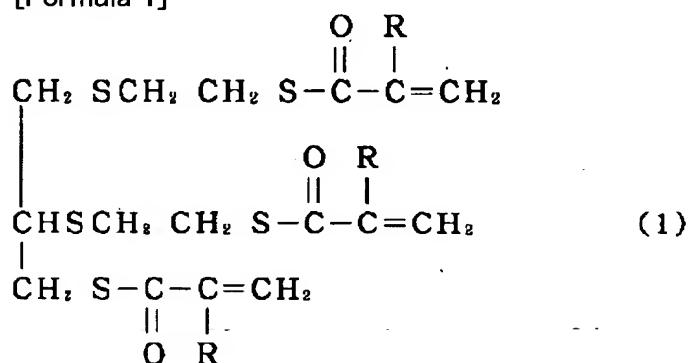
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 CLAIMS

[Claim(s)]

[Claim 1] The sulfur-containing (meta) acrylate compound expressed with the following type (1) and (** 1).

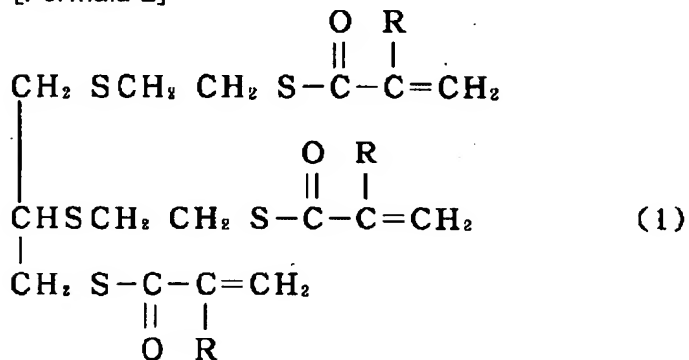
[Formula 1]



(R expresses a hydrogen atom or a methyl group among a formula)

[Claim 2] The polymerization nature constituent containing the sulfur-containing (meta) acrylate compound expressed with the following type (1) and (** 2).

[Formula 2]



(R expresses a hydrogen atom or a methyl group among a formula)

[Claim 3] The sulfur-containing (meta) acrylate compound expressed with a formula (1), and the polymerization nature constituent containing at least one sort of monomers which can be copolymerized according to claim 2.

[Claim 4] Sulfur-containing resin obtained by carrying out the polymerization of the constituent according to claim 2 or 3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the sulfur-containing resin which is made to carry out the polymerization of a new sulfur-containing (meta) acrylate compound, the polymerization nature constituent containing this compound, and its constituent, and is obtained. The sulfur-containing resin of this application is useful especially as a plastic lens which has good optical physical properties and a high refractive index, has the abrasion-proof nature which was very excellent, and is especially used for various optical lenses, such as a lens for glasses, etc.

[0002]

[Description of the Prior Art] A plastic lens is lightweight compared with an inorganic lens, cannot break easily, and since it can dye, it is spreading through optical elements, such as a spectacle lens and a camera lens, quickly in recent years. As resin widely used for current and these purposes, there are some to which the radical polymerization of the diethylene-glycol screw (allyl carbonate) (D.A.C is called hereafter) was carried out. This resin has the various descriptions -- workability, such as excelling in shock resistance, a lightweight thing, excelling in the dye affinity, cutting ability, and polish nature, is good. However, this resin has a refractive index as small as $n_D = 1.50$ compared with an inorganic lens ($n_D = 1.52$), in order to obtain an optical property equivalent to a glass lens, it is necessary to enlarge the main thickness of a lens, KOBA thickness, and curvature, and becoming thick on the whole is not avoided. For this reason, resin for lenses with a more high refractive index was desired.

[0003] D.A.C The polyurethane system lens is known as a lens with a refractive index higher than resin. this invention persons have proposed the polyurethane system lens which consists of a polymerization object of a xylylene diisocyanate compound and the Pori thiol compounds in JP,63-46213,A as this polyurethane system lens, and have spread widely as optical lenses, such as a lens for glasses. Moreover, the polyurethane system lens excellent in a light weight and shock resistance is proposed by JP,2-270859,A with the high refractive index with the combination of the specific Pori thiol compounds and an isocyanate compound. However, it has the fault that the lens by these resin does not have enough abrasion-proof nature, and the front face of a lens tends to get damaged. Moreover, in order to obtain a homogeneous lens optically, polymerization time

amount might become long, and workability might become complicated. For this reason, the further amelioration was desired that these troubles should be solved.
[0004]

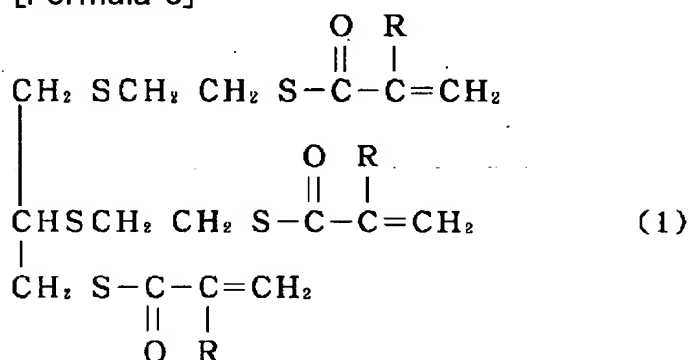
[Problem(s) to be Solved by the Invention] The purpose of this invention is offering a new sulfur-containing (meta) acrylate compound, and providing with useful resin especially the application of the lens which has good optical physical properties and a high refractive index, and has the abrasion-proof nature which was very excellent using this compound.

[0005]

[Means for Solving the Problem] this invention persons result in this invention, as a result of inquiring wholeheartedly, in order to solve an above-mentioned technical problem. That is, this invention relates to the sulfur-containing resin which is made to carry out the polymerization of the sulfur-containing (meta) acrylate compound expressed with the following type (1) and (** 3), the polymerization nature constituent containing the sulfur-containing (meta) acrylate compound expressed with a formula (1), and this constituent, and is obtained.

[0006]

[Formula 3]

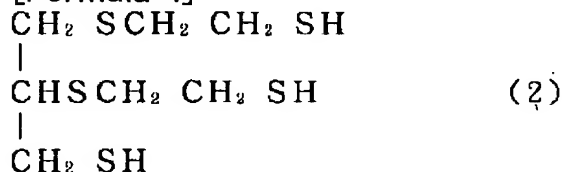


(R expresses a hydrogen atom or a methyl group among a formula)

Hereafter, this invention is explained to a detail. The sulfur-containing (meta) acrylate compound of this invention can manufacture a 1 expressed with following type (2) and (** 4), and 2-screw [(2-mercapto ethyl) thio]-3-mercapto propane as a start raw material.

[0007]

[Formula 4]



The Pori thiol compounds expressed with a formula (2) are easily manufactured by the approach to which make the approach of a publication, i.e., epihalohydrin and 2-mercaptoethanol, react to JP,2-270859,A, and thiourea is subsequently made to react.

[0008] The sulfur-containing (meta) acrylate compound expressed with a formula (1) ** The approach to which 3-4.5-mol acrylic-acid (meta) chloride etc. is made

to react at -20 degrees C – 60 degrees C to one mol of Pori thiol compounds expressed with a formula (2), 3–4.5–mol beta-chloro propionyl chloride or beta-chloro-alpha-methyl propionyl chloride is made to react at -20 degrees C – 80 degrees C to one mol of Pori thiol compounds expressed with ** type (2). Or subsequently It is manufactured by the approach to which a 3–6–mol base is made to react at -20 degrees C – 60 degrees C.

[0009] In order to remove the hydrogen chloride generated in the case of a reaction, it is necessary to make a base live together as a hydrogen chloride supplement agent in the system of reaction at the above-mentioned reaction. Although especially the base as a hydrogen chloride supplement agent is not limited, alkylamine, such as a trimethylamine and triethylamine, a pyridine, a sodium hydroxide, a potassium hydroxide, etc. are mentioned as a base generally used. As a base used at the reaction of the latter part of the aforementioned **, alkylamine, such as a trimethylamine and triethylamine, is more desirable. Moreover, an organic solvent may be used if needed in the case of this reaction. Although especially the organic solvent used is not limited, what does not have the reactivity of raw materials required for a reaction can be used for it. As an organic solvent, ketones, such as ether, such as halogenated hydrocarbon, such as aliphatic series, such as a hexane, a heptane, the petroleum ether, benzene, toluene, and a xylene, or aromatic hydrocarbon, chloroform, a methylene chloride, and an ethylene chloride, diethylether, dioxane, and a tetrahydrofuran, an acetone, and a methyl ethyl ketone, N.N-dimethylformamide, etc. are mentioned, for example.

[0010] The polymerization nature constituent of this invention contains the sulfur-containing (meta) acrylate compound expressed with said formula (1), contains the sulfur-containing (meta) acrylate compound and this which are expressed with a formula (1), and at least one sort of the monomer which can be copolymerized, and has polymerization nature. 20% of the weight or more of the whole quantity of the monomer of a sulfur-containing (meta) acrylate compound and others — desirable — 40 % of the weight or more — more — desirable — 60 % of the weight or more — it is . [compound / which is expressed with a formula (1) in the case of the constituent containing other monomers / sulfur-containing (meta) acrylate] In order that the monomer in which the sulfur-containing (meta) acrylate compound of this invention and copolymerization are possible may adjust many physical properties, such as adjustment of optical physical properties, such as a refractive index, and shock resistance, specific gravity, in order to adjust the viscosity of a monomer, and the handling of others, it is chosen according to the purpose and especially limitation is not carried out. Moreover, one sort or two sorts or more can also be mixed and used for the monomer in which these copolymerization is possible.

[0011] As a monomer which can be copolymerized, for example Benzyl acrylate, benzyl methacrylate, Butoxy ethyl acrylate, butoxy methyl methacrylate, cyclohexyl acrylate, Cyclohexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxymethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, Phenoxy ethyl acrylate, phenoxy ethyl methacrylate, Phenyl methacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, Diethylene glycol diacrylate, diethylene-glycol dimethacrylate, Triethylene glycol diacrylate, triethylene glycol dimethacrylate,

Tetraethylene glycol diacrylate, tetraethylene glycol dimethacrylate, Polyethylene-glycol diacrylate, polyethylene glycol dimethacrylate, Neopentyl glycol diacrylate, neopentyl glycol dimethacrylate, Ethylene glycol bis-glycidyl acrylate, ethylene glycol bis-glycidyl methacrylate, Bisphenol A diacrylate, bisphenol A dimethacrylate, 2 and 2-screw (4-AKUROKISHI diethoxy phenyl) propane, 2, and 2-screw (4-meta-KUROKISHI diethoxy phenyl) propane, Trimethylolpropane triacrylate, trimethylolpropanetrimethacrylate, Glycerol diacrylate, glycerol dimethacrylate, a pentaerythritol thoria chestnut rate, Pentaerythritol tetraacrylate, pentaerythritol tetra-methacrylate, Methylthio acrylate, methylthio methacrylate, phenylthio acrylate, Benzyl thio methacrylate, xylylene dithiol diacrylate, Xylylene dithiol dimethacrylate, mercapto ethyl sulfide diacrylate, Mercapto ethyl sulfide dimethacrylate, diallyl phthalate, Diaryl terephthalate, diallyl isophthalate, diaryl carbonate, diethylene-glycol bisallyl carbonate, styrene, chloro styrene, methyl styrene, bromostyrene, dibromo styrene, etc. are mentioned.

[0012] The sulfur-containing resin of this invention carries out the polymerization of said constituent, is obtained, and carries out copolymerization to the thing to which the polymerization of the sulfur-containing (meta) acrylate compound of this invention was carried out independently, or the monomer which can copolymerize [other] a sulfur-containing (meta) acrylate compound. Especially as a polymerization method for obtaining the sulfur-containing resin of this invention, it is not limited and the well-known radical polymerization approach can be taken. As a polymerization initiation means in this case, the exposures of use of radical initiators, such as various peroxides and an azo compound, or ultraviolet rays, a visible ray, alpha rays, beta rays, a gamma ray, an electron ray, etc. or these concomitant use are mentioned.

[0013] A well-known thing can be used as a radical initiator. As a typical thing Benzoyl peroxide, dicumyl peroxide, lauroyl peroxide, A G t-butyl par OKISHIAZE rate, t-butylperoxy-2-ethylhexanoate, T-butyl peroxy laurate, t-butyl peroxybenzoate, T-butylperoxy-3,5,5-trimethyl hexanoate, t-butyl peroxyacetate, Azo compounds, such as peroxides, such as screw (4-t-butyl cyclohexyl) peroxi dicarbonate and t-butylperoxyisopropylcarbonate, and azobisisobutyronitril, etc. are mentioned.

[0014] When irradiating ultraviolet rays etc. and making a polymerization start, a well-known sensitizer etc. can also be used. As a typical thing of a sensitizer, it is benzophenone, 4, and 4-diethylamino benzophenone, 1-hydroxy cyclohexyl phenyl ketone, p-dimethylamino isoamyl benzoate, 4-dimethylamino methyl benzoate, benzoin, benzoin ethyl ether, benzoin-isobutyl-ether, benzoin-iso-propyl-ether, 2, and 2-diethoxy acetophenone, methyl o-benzoylbenzoate, and 2-hydroxy. - 2-methyl-1-phenyl propane-1-ON, acyl phosphine oxide, etc. are mentioned.

[0015] A casting polymerization is mentioned as a typical polymerization method at the time of obtaining the sulfur-containing resin (for example, plastic lens) of this invention. That is, the polymerization nature constituent (it is also called monomer mixture) of this invention containing a radical initiator, a sensitizer, or these both is poured in between the mold held on the gasket or the tape. At this time, if needed, even if it processes degassing etc., there is no inconvenience in any way.

Subsequently, ultraviolet rays etc. are irradiated, it can heat in oven, or these can

be used together and stiffened, and the sulfur-containing resin of this invention can be obtained.

[0016] The polymerization method for obtaining the sulfur-containing resin of this invention, polymerization conditions, etc. cannot generally be limited with classes, such as an initiator to be used, an amount, and the class or rate of a monomer. For example, since it chooses the optimal temperature conditions in heating in oven since cooling etc. is processed in order to prevent overheating of monomer mixture when irradiating ultraviolet rays etc. and, temperature control may be carried out. When heating in oven, the method of heating gradually from low temperature, holding at an elevated temperature generally, and completing a polymerization is adopted. Moreover, since it is influenced also about the time amount of a polymerization with classes, such as an initiator to be used, an amount, and the class and rate of a monomer, it cannot generally limit. Generally, it is possible to aim at compaction of polymerization time amount by the exposure of ultraviolet rays etc. In case the sulfur-containing resin of this invention is obtained, according to the purpose, various matter, such as a chain elongation agent, a cross linking agent, light stabilizer, an ultraviolet ray absorbent, an antioxidant, the oil color, and a bulking agent, may be similarly added in the well-known fabricating method. Moreover, about the taken-out sulfur-containing resin, annealing etc. may be processed if needed.

[0017] The sulfur-containing resin obtained using the sulfur-containing (meta) acrylate of this invention is low distribution in a high refractive index, and has the description which was excellent in thermal resistance and weatherability and was very excellent in especially abrasion-proof nature. By changing the mold at the time of a casting polymerization, the sulfur-containing resin of this invention can be obtained as a Plastic solid of various gestalten, and can be used for various kinds of applications as optical element materials, such as a spectacle lens and a camera lens, and transparence resin. Especially, it is suitable as optical element materials, such as a spectacle lens and a camera lens. Furthermore, with the lens using the sulfur-containing resin of this invention, since acid resisting, high degree-of-hardness grant, wear-resistant improvement, chemical-resistant improvement, fog resistance grant, or fashionability grant is improved if needed, physical or chemical preparation, such as surface polish, antistatic treatment, rebound ace court processing, nonreflective coat processing, dyeing processing, and modulated light processing, can also be performed.

[0018]

[Example] Hereafter, an example and the example of a comparison explain this invention concretely. In addition, the following examining methods estimated a refractive index, the Abbe number, abrasion-proof nature, an appearance, and shock resistance among the performance tests of the acquired sulfur-containing resin Plastic solid.

- A refractive index, the Abbe number : it measured at 20 degrees C using Pulfrich refractometer.

- Abrasion-proof nature : the front face of resin was rubbed by the steel wool of #0000, the surface difficulty of getting damaged was investigated, and it judged as follows.

[0019] O : -- **: which does not get damaged at all even if it rubs strongly -- x: which will get damaged a little if it rubs strongly -- outside of - to which weak friction also gets damaged It saw and observed by :viewing.

- Shock resistance : the iron ball was dropped from height of 127cm to a part for the core of the produced lens, and shock resistance was evaluated to it.

[0020] 1 and 2-screw [(2-mercapto ethyl) thio]-3-mercapto propane 52.10g (0.20 mols) and acetone 300ml were taught to the reaction flask of 4 openings which attached example 1 stirring rod, the thermometer, and the dropping funnel, and after dropping 132g of NaOH water solutions 20% and fully stirring, cooling and stirring at 10 degrees C or less, beta-chloropropionic acid chloride 83.80g (0.66 mols) was dropped gradually. It stirred at 10 more degrees C after dropping termination for 4 hours. Subsequently, triethylamine 66.79g (0.66 mols) was dropped gradually, cooling and stirring at 10 degrees C or less. It stirred at 25 more degrees C after dropping termination for 4 hours. Then, after dropping the hydrochloric-acid water solution gradually 10% and making the inside of the system of reaction into acidity, toluene 300ml and 200ml of water were added, and the resultant was extracted in the organic layer. After separating liquids and removing a water layer, it washed 3 times with water further. After drying a toluene layer with sulfuric anhydride magnesium, it distilled off under reduced pressure of toluene and 63.56g of the transparent and colorless target sulfur-containing acrylate compounds was obtained. This thing The chart of $^1\text{H-NMR}$ (CDCl_3 the inside of a solvent, tetramethylsilane criteria) was shown in (drawing 1).

[0021] 1 and 2-screw [(2-mercapto ethyl) thio]-3-mercapto propane 52.10g (0.20 mols) and acetone 300ml were taught to the reaction flask of 4 openings which attached example 2 stirring rod, the thermometer, and the dropping funnel, and after dropping 132g of NaOH water solutions 20% and fully stirring, cooling and stirring at 10 degrees C or less, methacrylic-acid chloride 68.99g (0.66 mols) was dropped gradually. It stirred after dropping termination for further 4 hours. Then, toluene 300ml and 200ml of water were added, and the resultant was extracted in the organic layer. After separating liquids, removing a water layer and the rare sodium-hydrogencarbonate water solution washed the toluene layer, it washed 3 times with water further. After drying a toluene layer with sulfuric anhydride magnesium, it distilled off under reduced pressure of toluene and 74.17g of the transparent and colorless target sulfur-containing methacrylate compounds was obtained. This thing The chart of $^1\text{H-NMR}$ (CDCl_3 the inside of a solvent, tetramethylsilane criteria) was shown in (drawing 2).

[0022] It is 2-hydroxy as 25mg of t-butylperoxy-2-ethylhexanoate, and a sensitizer as a radical polymerization initiator to 50g of sulfur-containing acrylate compounds obtained in the example 3 example 1. - 2 - Methyl-1-phenyl propane-1-ON 50mg could be added, and it mixed. It poured into the mold mold which consists of glass mold and a gasket, after fully carrying out degassing of this. After irradiating ultraviolet rays for 5 minutes, cooling, the temperature up was carried out over 1 hour from 30 degrees C to 120 degrees C, and it heated at 120 more degrees C for 1 hour. After polymerization termination, it cooled gradually and the Plastic solid was taken out from mold. The acquired Plastic solid (lens) was transparent and colorless, and were refractive-index $n_d = 1.645$ and Abbe number $n_{ud} = 35$.

Moreover, it excelled also in abrasion-proof nature very much, and evaluation was O.

[0023] To 50g of sulfur-containing methacrylate compounds obtained in the example 4 example 2, 50mg of t-butylperoxy2-ethylhexanoate could be added as a radical polymerization initiator, and it mixed. It poured into the mold mold which consists of glass mold and a gasket, after fully carrying out degassing of this. The temperature up was carried out over 2 hours from 30 degrees C to 120 degrees C, and it heated at 120 more degrees C for 1 hour. After polymerization termination, it cooled gradually and the Plastic solid was taken out from mold. The acquired Plastic solid (lens) was transparent and colorless, and were refractive-index $n_d = 1.628$ and Abbe number $n_{ud} = 37$. It excelled also in abrasion-proof nature and evaluation was O.

[0024] It is 2-hydroxy as 50mg of t-butylperoxy2-ethylhexanoate, and a sensitizer to 35g of sulfur-containing acrylate compounds obtained in the example 5 example 1 as polyethylene-glycol-dimethacrylate (NK ester 9 by Shin-Nakamura Chemical Co., Ltd. $n = 9$, G) 15g, and a radical polymerization initiator. - 2 - Methyl-1-phenyl propane-1-ON 100mg could be added, and it mixed. It poured into the mold mold which consists of glass mold and a gasket, after fully carrying out degassing of this. Since the viscosity of monomer mixture was low as compared with an example 3, impregnation was easy. After irradiating ultraviolet rays for 5 minutes, cooling, the temperature up was carried out over 1 hour from 30 degrees C to 120 degrees C, and it heated at 120 more degrees C for 1 hour. After polymerization termination, it cooled gradually and the Plastic solid was taken out from mold. The acquired Plastic solid (lens) was transparent and colorless, and refractive-index $n_d = 1.594$, Abbe number $n_{ud} = 41$, and specific gravity were 1.31. It excelled also in abrasion-proof nature very much, and evaluation was O. Moreover, shock resistance was improving rather than the Plastic solid acquired in the example 3.

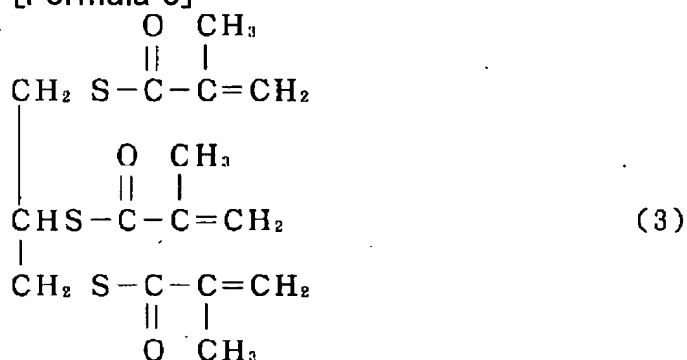
[0025] It is 2-hydroxy as 60mg of t-butylperoxy2-ethylhexanoate, and a sensitizer to 32g of sulfur-containing methacrylate compounds obtained in the example 6 example 2 as tetraethylene glycol dimethacrylate (NK ester 4 by Shin-Nakamura Chemical Co., Ltd. $n = 4$, G) 8g, and a radical polymerization initiator. - 2 - Methyl-1-phenyl propane-1-ON 80mg could be added, and it mixed. It poured into the mold mold which consists of glass mold and a gasket, after fully carrying out degassing of this. Since the viscosity of monomer mixture was low as compared with an example 4, impregnation was easy. After irradiating ultraviolet rays for 7 minutes, cooling, the temperature up was carried out over 1 hour from 30 degrees C to 120 degrees C, and it heated at 120 more degrees C for 1 hour. After polymerization termination, it cooled gradually and the Plastic solid was taken out from mold. The acquired Plastic solid (lens) was transparent and colorless, and refractive-index $n_d = 1.599$, Abbe number $n_{ud} = 40$, and specific gravity were 1.31. It excelled also in abrasion-proof nature and evaluation was O. Moreover, shock resistance was improving rather than the Plastic solid acquired in the example 4.

[0026] To 50g of sulfur-containing methacrylate compounds expressed with the example of comparison 1 following type (3), and (** 5), 0.5g of t-butylperoxy2-ethylhexanoate could be added as a radical polymerization initiator, and it mixed. It poured into the mold mold which consists of glass mold and a gasket, after fully

carrying out degassing of this. The temperature up was carried out over 2 hours from 30 degrees C to 120 degrees C, and it heated at 120 more degrees C for 1 hour. After polymerization termination, it cooled gradually and the Plastic solid was taken out from mold. The acquired Plastic solid (lens) is transparent and colorless, and are refractive-index $n_d = 1.607$ and Abbe number $n_{ud} = 35$, and a refractive index and the Abbe number were inferior in it as compared with examples 3 and 4. Moreover, evaluation of abrasion-proof nature was **.

[0027]

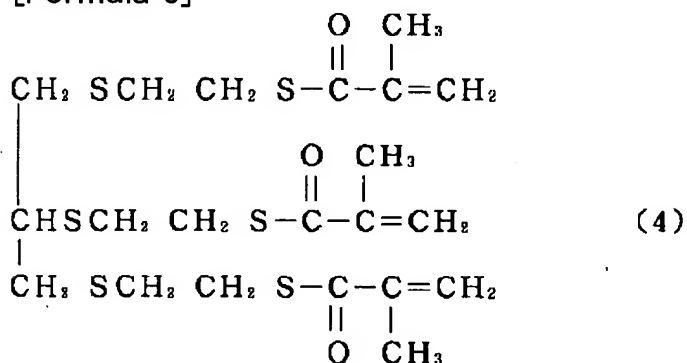
[Formula 5]



[0028] To 50g of sulfur-containing methacrylate compounds expressed with the example of comparison 2 following type (4), and (** 6), 0.5g of t-butylperoxy2-ethylhexanoate could be added as a radical polymerization initiator, and it mixed. It poured into the mold mold which consists of glass mold and a gasket, after fully carrying out degassing of this. The temperature up was carried out over 2 hours from 30 degrees C to 120 degrees C, and it heated at 120 more degrees C for 1 hour. After polymerization termination, it cooled gradually and the Plastic solid was taken out from mold. The acquired Plastic solid (lens) is transparent and colorless, and are refractive-index $n_d = 1.620$ and Abbe number $n_{ud} = 34$, and a refractive index and the Abbe number were inferior in it as compared with examples 3 and 4. Moreover, evaluation of abrasion-proof nature was **.

[0029]

[Formula 6]



[0030]

[Effect of the Invention] Especially, the sulfur-containing (meta) acrylate compound of this invention has good optical physical properties and a high refractive index, and gives a plastic lens with the abrasion-proof nature which was

very excellent.

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